A Standardized Approach for Estimating the Permeability of Plastic Films to Soil Fumigants under Various Field and Environmental Conditions

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Minimizing atmospheric emissions of soil fumigants is critical for protecting human and environmental health. Covering the soil surface with a plastic tarp is a common approach to restrict fumigant emissions. The mass transfer of the fumigant vapors through the tarp is often the rate-limiting factor in fumigant emissions. An approach for standardizing measurements of film permeability is proposed that is based on determining the resistance (R) of films to diffusion of fumigants. Using this approach, R values were determined for more than 200 film–chemical combinations under a range of temperature, relative humidity, and film handling conditions. Resistance to diffusion was specific for each fumigant/film combination, with the largest range of values observed for the fumigant chloropicrin. For each fumigant, R decreased with increasing temperature. Changes in film permeability due to increases in temperature or field installation were generally less than a factor of five. For one film, R values determined under conditions of very high relative humidity (~100%) were at least 100 times lower than when humidity was very low (~2%). This approach simplifies the selection of appropriate films for soil fumigation by providing rapid, reproducible, and precise measurements of their permeability to specific fumigants and application conditions.

Soil fumigants are used to control a broad range of soil-borne pests that affect production of many high-value crops. The use of the popular fumigant methyl bromide (MeBr) has been restricted or phased out in developed countries due to its ozone-depleting potential (USEPA, 2009a). This has led to an increased use of alternative soil fumigants, including 1,3-dichloropropene (1,3-D), methyl isothiocyanate (MITC) generators (e.g., dazomet and metam sodium), chloropicrin (CP), and iodomethane (methyl iodide [MeI]). Sulfuryl fluoride (SF) and dimethyl disulfide (DMDS) are also under consideration as potential alternative soil fumigants. Fumigants have relatively high vapor pressures, low boiling points, and high air–water partitioning coefficients; they are dispersed through the soil largely in the gas phase (Ruzo, 2006). Volatilization from the soil surface is an important consideration in determining human exposure and environmental contamination resulting from soil fumigation. Fumigant compounds are under investigation for their impacts on air quality, and the continued use of soil fumigants will likely be subject to increasingly stringent restrictions, including expanded buffer zones and set-backs surrounding treated areas, the use of additional personal protective equipment by field workers and applicators, fumigant management plans, and regulation of plastic tarps (USEPA, 2009b). Some states, such as California, impose additional restrictions on soil fumigation and have not registered MeI as a fumigant.

Controlling fumigant emissions to the atmosphere is critical for their continued use as a pre-plant soil treatment. One emissions-reduction strategy is the use of plastic tarps to cover the soil surface after fumigation. Current fumigation practices in the United States typically use low-density polyethylene (LDPE) or high-density polyethylene (HDPE) tarps. Polyethylene tarps are permeable to organic vapors and generally do not result in large reductions in total fumigant emissions. Measurements of MeBr volatilization are variable, but many field studies have indicated that MeBr volatilization from bare soil may be ~90% of the applied MeBr mass, decreasing to ~60% or less with the use of a polyethylene tarp (Yates et al., 2003). The fumigant compounds

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Abbreviations: CP, chloropicrin; 1,3-D, 1,3-dichloropropene; DMDS, dimethyl disulfide; HDPE, high-density polyethylene; LDPE, low-density polyethylene; MeBr, methyl bromide; MeI, methyl iodide; MITC, methyl isothiocyanate; RH, relative humidity; SF, sulfuryl fluoride; VIF, virtually impermeable film.

1,3-D and CP were transported more rapidly than MeBr through HDPE (Papiernik et al., 2001). Tarping the soil surface with HDPE decreased emissions of 1,3-D from 56 to 48% (Gan et al., 1998) and reduced CP emissions from 82 to 20% in laboratory columns (Gan et al., 2000). The larger decrease in CP emissions is probably due to the rapid transformation of CP in soil; CP half-lives of <1 to 4 d have been reported in different soils at 20°C (Gan et al., 2000). For compounds that are rapidly degraded in soil, even relatively inefficient diffusion barriers can result in appreciable reductions in emissions.

Coextruded films containing ethylene vinyl alcohol or polyamide (nylon), commonly referred to as virtually impermeable films (VIF), can be much more effective than polyethylene at containing fumigants (Austerweil et al., 2006; Gamliel et al., 1998a,b; Wang et al., 1999). Some studies have indicated that fumigant emissions can be drastically decreased by VIF when the film remains on the soil surface long enough to allow for complete degradation of the compound in the soil. For example, in field experiments using broadcast application, using VIF instead of HDPE reduced MeBr emissions from >50 to <5% (Wang et al., 1997), 1,3-D emissions from 33 to ~7% (Gao and Trout, 2007), and CP emissions from 9 to 1% (Gao and Trout, 2007). With more effective containment, adequate efficacy may be achieved with lower fumigant application rates (Chellemi and Mirusso, 2006; Gamliel et al., 1998b; Gilreath et al., 2005; Wang et al., 1997). In contrast, other studies have shown that fumigant emissions are not always appreciably reduced using films designated as VIF. For example, in a field study, CP emissions from beds tarped with VIF (16%) were about the same as those from beds tarped with LDPE (18%) (Qin et al., 2008). In another field study, Wang and Yates (1998) estimated that emissions of MeBr from beds tarped with VIF (90%) were nearly as high as from beds tarped with standard HDPE (95%).

Volatilization of soil-applied fumigants is dependent on many factors, including climatic variables, soil conditions, the rate of fumigant degradation in the soil, application methods, and surface cover (film type, extent of coverage, and cover time). These factors may be interdependent; for example, increasing temperature increases the rate of gaseous diffusion in the soil, increases the rate of transfer of fumigant vapors through the plastic film, and generally increases the rate of fumigant degradation in soil (Yates et al., 2003). Prediction of fumigant volatilization rates is complicated by concurrent interrelated processes. In tarped fields, the mass transfer of fumigant vapors through the plastic film may often be the rate-limiting factor in fumigant emissions, so that an accurate estimate of film permeability may greatly increase the reliability of predictions of fumigant volatilization.

A method for estimating mass transfer coefficients (h) of fumigant compounds across plastic films has been developed (Papiernik et al., 2001, 2002). The h, unlike other measures of permeability, is a property of the film–chemical combination and is independent of the concentration gradient across the film (Papiernik et al., 2001). The inverse of h is R:

$$R = 1/h \qquad [1]$$

The R indicates the resistance to diffusion and is analogous to a thermal insulation value. A higher R value indicates a better diffusion barrier. We propose that this approach be used as a standard measure of permeability of films used in soil fumigation. Once R and degradation rate are known, cumulative fumigant emissions from tarped soil can be predicted by using commonly available methods to estimate the soil diffusion coefficient (Reid et al., 1987).

Ethylene vinyl alcohol and polyamide polymers are often used in films for food packaging to exclude oxygen and retain volatile flavor compounds. These polymers are also often used in the manufacture of low-permeability agricultural films. Relative humidity can affect the flexibility and fragility of films made of these polymers (Lagarón et al., 2001) and their permeability to oxygen (Aucejo et al., 2000; Lagarón et al., 2003; Muramatsu et al., 2003) and other vapors (Johansson and Leufvén, 1994). Research on the permeability of plastic films has shown that the effect of relative humidity on gas transport through plastic films is compound- and film specific (Johansson and Leufvén, 1994) and varies with temperature (Muramatsu et al., 2003). Agricultural films can be exposed to high humidity during soil fumigation, so it is important to characterize the affect of relative humidity on film permeability to fumigant vapors.

In these experiments, we demonstrate that the determination of R gives rapid, reproducible, and precise measurements of film permeability. We use this robust method to determine the transport of various fumigant compounds through a wide variety of polyethylene and other films and evaluate the impact of film handling, temperature, and relative humidity on film permeability. The large number of film–fumigant combinations tested in this study provides a much larger data set than was previously available regarding the permeability of plastic films to fumigant vapors.

Materials and Methods

Chemicals

Methyl bromide in a pressurized gas cylinder (>99% purity) was obtained from Soil Chemical Corporation Products (Holister, CA). Standards of CP (99.9% purity) (Trinity Manufacturing, Inc., Hamlet, NC), 1,3-dichloropropene (49.19% cis, 49.68% trans) (Dow Agrosciences, Indianapolis, IN), MITC (98% purity) (Fluka Specialty Chemicals, Inc., St. Louis, MO), MeI (99.7% purity) (Sigma Aldrich, Inc., St. Louis, MO), sulfuryl fluoride (99% purity) (Dow Agrosciences), and dimethyl disulfide (99% purity) (Sigma Aldrich, Inc.) were used as supplied.

Plastic Films

Film samples were obtained from the plastic manufacturers or distributors and from 29 field demonstration trials affiliated with the USDA–ARS Area-Wide Pest Management Project for Alternatives to Methyl Bromide (Chellemi and Browne, 2006). The field trials were conducted in Florida, Georgia, North Carolina, South Carolina, Alabama, and Virginia by commercial vegetable, ornamental, and forest seedling nursery growers and commercial fumigant applicators. These trials included a broad range of cultural, physical, and environmental conditions and a variety of commonly used film types. Film samples were taken directly from the roll before field application and from the field after their application. Field samples were collected <48 h after application from an untreated (no fumigant) section to assess the impact of application methods and equipment on subsequent permeability to fumigants. All area-wide samples were carefully placed in a protective shipping container and expedited to the USDA-ARS U.S. Salinity Laboratory in Riverside, California for testing. A description of the films tested is provided in Supplementary Table S1.

Determination of Film Permeability

Details of the apparatus, procedures, and analysis are given elsewhere (Papiernik et al., 2001, 2002). Permeability was determined in static sealed cells in which fumigant vapor was spiked to one side of the film and the concentrations on both sides of the film were monitored over time, preferably until equilibrium. An analytical model was fitted to the data to obtain h, and the R the value was calculated as the inverse of h. This model relies on a mass balance approach and includes sorption to and diffusion across the film membrane. All tests were conducted in triplicate. Experiments were conducted in controlled temperature rooms with variation of ±0.5°C. All equipment was equilibrated at the experimental temperature before each experiment was initiated.

Effect of Relative Humidity on Film Permeability

The effect of relative humidity (RH) on the measured permeability was tested by adjusting the humidity of each side of the film. To reduce the RH to approximately 2%, a glass column packed with Drierite (Hammond Drierite Co., Xenia, OH) (anhydrous $CaSO_4$) was connected to one side of the sealed cell, and a low flow rate of dried air was allowed to pass through the cell for several minutes. The RH of the air exiting the sealed cell was measured using a relative humidity and temperature sensor (model CS-215; Campbell Scientific, Logan, UT). The rated accuracy (at 25°C) of this device is ±2% for 10% < RH < 90% and ±4% for RH < 10% and RH > 90%. For high RH (e.g., >90%), a pipette was used to place a 75-µL water droplet on one side of the sealed cell approximately 24 h before spiking with fumigants. Preliminary tests showed that after 24 h, the drop was visible but was of miniscule size. It was presumed that the saturated water vapor density reached the equilibrium value and that the remaining water had a negligible effect on the fumigant concentration. For RH values between dry and saturation, the RH in the cell was taken as the ambient RH in the laboratory recorded when the permeation cells were prepared. Typically, the ambient RH values in the laboratory varied from 30 to 50%.

Results and Discussion

Effect of Fumigant–Film Combination on Resistance

Variation in film permeability has been observed to a limited extent previously (Papiernik et al., 2001; Papiernik and Yates, 2002), but the wide variety of fumigant–film combinations tested in this study shows a very large range in permeability. When grouped by film type, R values were greatest for films grouped as VIF, intermediate for metalized films, and lowest for polyethylene films (Fig. 1; Supplementary Table S2). However, for each individual film tested, the resistance to diffusion varied depending on the fumigant tested. An illustration of the variation due to specific fumigants tested is presented for a typical VIF and LDPE (Fig. 2). The high degree of chemical specificity among fumigant–film combinations is demonstrated by dif-

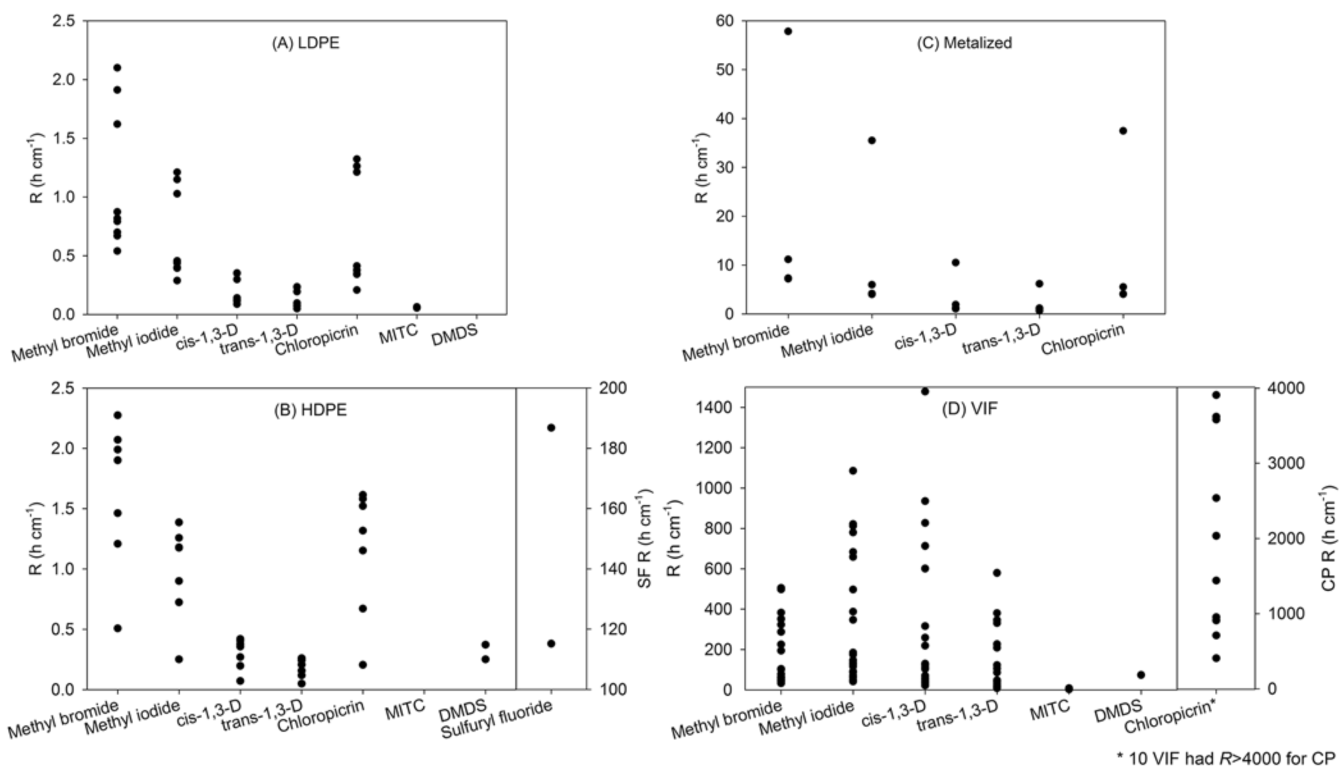

Fig. 1. Variation in the resistance to diffusion (*R*) at 25°C of plastic films used in the Area-Wide Pest Management Project for each film type. All films were sampled directly from the roll with no field handling. HDPE, high-density polyethylene; LDPE, low-density polyethylene; VIF, virtually impermeable films.

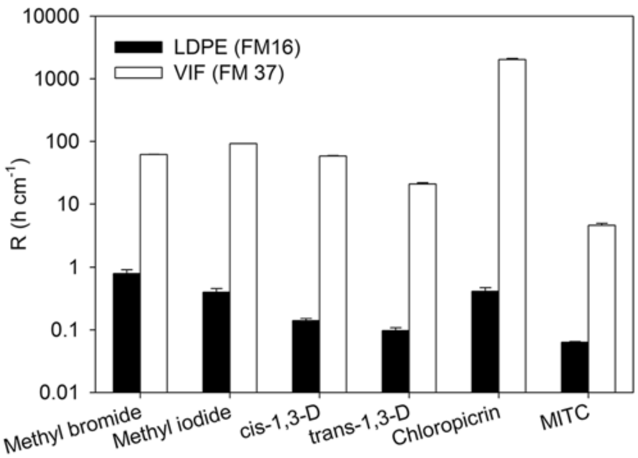

Fig. 2. Resistance to diffusion (*R*) values determined at 25°C for six fumigant compounds through two films with no field handling. Values are the mean of triplicate cells; error bars indicate SE. Note that *y* axis is log scale. LDPE, low-density polyethylene; MITC, methyl isothiocyanate; VIF, virtually impermeable film.

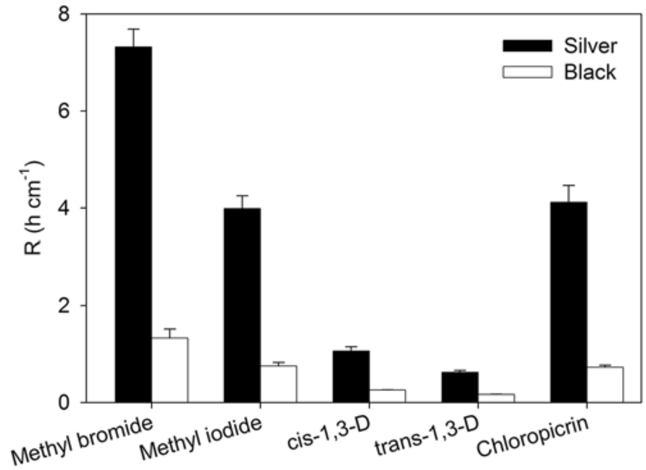

Fig. 3. Variation in resistance to diffusion (*R*) factors for the transport of five fumigant compounds through different portions of a mixed composition film (silver indicates metalized and black low-density polyethylene). Values are the mean of three replicate cells; error bars indicate SE. All values determined for film with no field handling at 25°C.

ferences in the resistance to diffusion of 1,3-D isomers: trans-1,3-D was consistently transported through the film faster than cis-1,3-D. The *R* value of trans-1,3-D was on average 2.5 less than the *R* value of cis-1,3-D for VIF and 1.6 times less for metalized and polyethylene films (Fig. 1–3). For an LDPE film with metalized sections (FM19), the metalized portion of the film had *R* values that were 3 to 7 times those of the nonmetalized black LDPE portion of the same film (Fig. 3).

Higher-permeability films (those with low *R* values) tended to be more permeable to alternative fumigants than to MeBr (Fig. 1A–1C), as was previously observed for HDPE (Papiernik and Yates, 2002). The VIF tested generally showed higher resistance to diffusion of MeI, 1,3-D, and CP than to MeBr (Fig. 1D). Thus, a greater disparity in fumigant barrier properties was observed between VIF and the other film types for MeI, 1,3-D isomers, and CP. For MeBr, the average *R* value of 180 h cm^{-1} in the VIF group was 10 and >100 times greater than average *R* values for metalized and HDPE films, respectively. For MeI and 1,3-D, the average *R* value observed for the VIF group was hundreds of times greater than the average *R* value for polyethylene films and 30 to 80 times greater than the average *R* value for metalized films. The largest discrepancy was observed for CP, for which many VIF presented a nearly complete barrier to fumigant diffusion, with mean *R* values being several orders of magnitude greater than those for metalized or polyethylene films (Fig. 1D). Film permeability to MITC was higher than to other fumigants, which is consistent with previous observations (Austerweil et al., 2006). For all eight films tested, MITC *R* values were <10 h cm^{-1} (Fig. 1 and 2). Because a film can have widely disparate permeability to different fumigants (Fig. 2; Supplementary Table S2), it is important to determine *R* values for each film–chemical combination to accurately predict the effectiveness of a particular film in containing fumigants.

This study is the first to describe the permeability of a range of plastic films to SF and DMDS. Permeability of four polyethylene films to DMDS was similar to that for 1,3-D, and the permeability of two VIF to DMDS was similar to MeBr and MeI (Supplementary Table S2). All tested films showed low permeability to SF, with *R* values >100 h cm^{-1}, much higher than those for other fumigants (Fig. 1B; Supplementary Table S2). The two HDPE films tested had barrier properties to SF (*R* = 115 and 187 h cm^{-1}) that approached the barrier properties of VIF to MeBr (mean *R* = 180 h cm^{-1}). Four VIF had very high *R* values for SF (>3900 h cm^{-1}) (Supplementary Table S2). These limited results suggest that plastic tarps contain SF more effectively than other fumigants.

The response of VIF as a barrier to the diffusion of fumigant vapors is highly variable (Fig. 1D), indicating that the term VIF is not quantitative as it is currently used. For most fumigants, the coefficient of variation of *R* values was >100% for metalized films and VIF. The observed wide variation in *R* values suggests that it may be difficult to predict the permeability of plastic films to fumigant vapors a priori and support the need for a simple reliable method to measure film permeability. This observed variation in *R* for VIF also suggests that it may be inadvisable to use VIF or other general terms as descriptors of plastic permeability as the basis for buffer zones and other regulations. The use of a quantitative measure such as *R* provides a means by which to predict fumigant emissions for a specific film–chemical combination under a given set of environmental conditions.

Resistance Varies with Temperature

The temperature response of films of widely varying permeability was determined. In all cases, *R* decreased with increasing temperature from 15 to 35°C (Fig. 4; Table 1). Previous research has consistently shown that the permeability of polyethylene films to fumigants increases with increasing temperature (Gamliel et al., 1998a; Kolbezen and Abu-El-Haj, 1977; Papiernik and Yates, 2002). The change in film permeability with temperature was determined using the Arrhenius equation (Fig. 4). The activation energies determined by regression ranged from −18 to −108 kJ mol^{-1} (Supplementary Table S3). For all fumigants, the activation energy was higher for VIF than for polyethylene films, indicating that temperature has a larger effect on the permeability of VIF than polyethylene

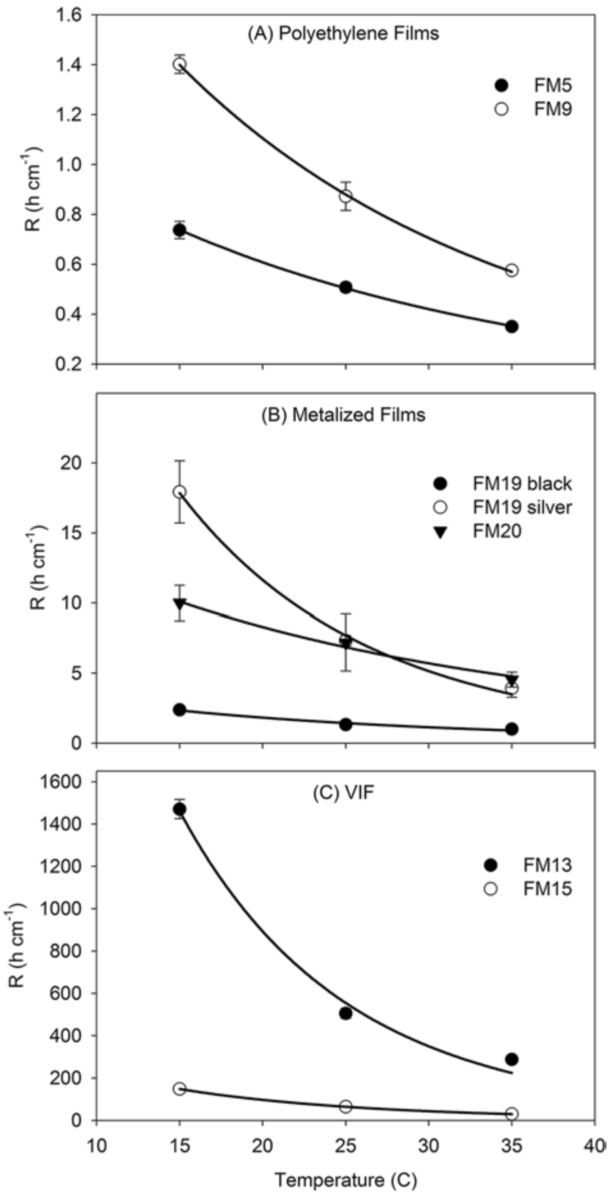

Fig. 4. Temperature response of the resistance (*R*) of various films to methyl bromide diffusion. Values are the mean of triplicate measurements; error bars indicate SE. Lines indicate fit of the Arrhenius equation to the data. VIF, virtually impermeable films.

films. For VIF, *R* values increased by a factor of 2 to 3 for each 10°C decrease from 35 to 15°C. For the HDPE and LDPE films tested, the *R* value increased by an average of 1.5 times for each 10°C decrease. These changes in permeability of polyethylene were consistent with previous reports showing that that fumigant *R* values increased by 1.4 to 1.9 times for each 10°C decrease in temperature from 20 to 40°C (Papiernik and Yates, 2002). For all films, temperature had a stronger effect on *R* at lower temperatures (Fig. 4).

Resistance Can Vary with Film Handling

Field deployment generally had a small effect on the transport of five fumigants through 34 films, with *R* values ranging over 3 to 5 orders of magnitude (Supplementary Table S4). Similarly, *R* values were approximately the same for MITC and DMDS before and after field installation. For polyethylene films (n = 10), the *R* values for all fumigants determined after installation in the field ranged from 73 to 149% of that determined for the film taken directly from the roll with no installation in the field, with a mean ratio of 0.97. These results are consistent with previous reports that field handling has a small effect on the permeability of polyethylene films (Papiernik and Yates, 2002; Qin et al., 2008). Film handing had a large effect on *R* values for some film–fumigant combinations. For the three metalized films tested, the field *R*/roll *R* ranged from 0.14 to 1.04, with a mean ratio of 0.62, indicating that for one metalized film (FM74), field deployment decreased the *R* value by a factor of 7. Films with low permeability, as a class, exhibited the largest decrease in *R* value as a result of field handling, but the response of individual films was variable. For the VIF tested, the field *R*/roll *R* ranged from 0.2 to 2.2 (Fig. 5), with a mean ratio of 0.8 to 0.9 for each fumigant. The response of film permeability to CP was more variable than for the other fumigants tested (Fig. 5). Qin et al. (2008) reported a very large increase in permeability of a VIF to CP after installation in the field.

Films can be stretched, punctured, torn, affected by ultraviolet light, or otherwise disrupted during the soil fumigation period. These tests were conducted on film samples that appeared intact (i.e., there were no obvious holes). The results of these paired measurements indicate that for many films, field deployment is not expected to result in a large change in permeability as long as the film maintains its physical integrity. Under similar conditions of film handling, the permeability of some films was affected by field deployment, even with no obvious disruptions in the film's continuity. The response of films to field application is highly variable and likely depends on the characteristics of the film and the environmental conditions, such as relative humidity.

Resistance of a Virtually Impermeable Film Varies with Relative Humidity

Previous research showed that condensed water, even a continuous layer, did not affect the mass transfer of fumigants through a HDPE film (Papiernik and Yates, 2002). Relative humidity had a large impact on the permeability of a VIF (FM4) to five fumigants (Table 2). For this film, when the RH was 100% on either side of the film, the *R* was at least 100 times lower than when RH was very low (Table 2). In the standard test, in which films were tested with ambient RH on both sides of the film, *R* values for each fumigant were intermediate between the extremes reported in Table 2 (Supplementary Table S2). At high humidity, the permeability of this VIF to fumigant vapors was of similar magnitude as the permeability of a polyethylene film.

The decreased effectiveness of some VIF under conditions of high humidity may help explain the apparent inconsistent performance of VIF in controlling fumigant emissions after soil fumigation. During the soil fumigation period, the RH on both sides of the film varies with atmospheric and soil conditions. Relative humidity is expected to be high on the underside of the film when fumigation occurs in moist soil or when fumigants are applied with water under the tarp (e.g., through drip irrigation lines). In these experiments, the film

Table 1. Temperature response of resistance to diffusion (R) of selected films to five fumigant compounds. For chloropicrin values not quantified, the lower limit was calculated from Eq. [2], using the maximum observed value of f and the duration of the experiment as t_0.

Film ID†	Temp.	*R* value				
		Methyl bromide	Methyl iodide	cis-1,3-D	trans-1,3-D	Chloropicrin
	°C	h cm⁻¹				
FM5	15	0.74 ± 0.03‡	0.39 ± 0.02	0.09 ± 0.00	0.06 ± 0.00	0.38 ± 0.02
HDPE	25	0.51 ± 0.02	0.25 ± 0.01	0.07 ± 0.00	0.05 ± 0.00	0.21 ± 0.02
	35	0.35 ± 0.00	0.19 ± 0.00	0.06 ± 0.00	0.04 ± 0.00	0.16 ± 0.00
FM9	15	1.40 ± 0.04	0.75 ± 0.04	0.18 ± 0.01	0.11 ± 0.01	0.78 ± 0.03
LDPE	25	0.87 ± 0.06	0.44 ± 0.03	0.09 ± 0.02	0.05 ± 0.02	0.34 ± 0.06
	35	0.58 ± 0.01	0.33 ± 0.01	0.10 ± 0.00	0.06 ± 0.00	0.29 ± 0.03
FM13	15	1470 ± 46	5,857 ± 409	8,275 ± 1,153	3048 ± 291	>15,000
VIF	25	505 ± 23	1,086 ± 25	1,478 ± 135	580 ± 43	>11,000
	35	288 ± 8	740 ± 26	1,288 ± 36	446 ± 12	>8,400
FM15	15	148 ± 5	269 ± 7	248 ± 17	89 ± 10	>15,000§
VIF	25	64 ± 2	116 ± 8	130 ± 2	46.8 ± 0.6	>7,200
	35	29.8 ± 0.6	50 ± 1	47 ± 2	18.6 ± 0.7	2,803 ± 542
FM19	15	2.38 ± 0.02	1.34 ± 0.02	0.37 ± 0.01	0.21 ± 0.01	1.54 ± 0.07
Black area	25	1.3 ± 0.2	0.75 ± 0.07	0.26 ± 0.00	0.17 ± 0.00	0.72 ± 0.04
	35	1.00 ± 0.00	0.56 ± 0.04	0.19 ± 0.01	0.13 ± 0.00	0.49 ± 0.05
FM19	15	18 ± 2	10 ± 1	2.6 ± 0.4	1.6 ± 0.2	8.9 ± 0.5
Silver area	25	7.3 ± 0.4	4.0 ± 0.3	1.06 ± 0.09	0.62 ± 0.04	4.1 ± 0.3
	35	3.9 ± 0.6	2.2 ± 0.3	0.7 ± 0.1	0.4 ± 0.1	1.7 ± 0.1
FM20	15	10 ± 1	5.8 ± 0.7	1.4 ± 0.2	0.81 ± 0.09	5.8 ± 0.6
Metalized	25	7 ± 2	4 ± 1	1.2 ± 0.3	0.93 ± 0.04	4 ± 1
	35	4.5 ± 0.5	2.7 ± 0.3	0.7 ± 0.1	0.47 ± 0.04	2.4 ± 0.2

† HDPE, high-density polyethylene; LDPE, low-density polyethylene; VIF, virtually impermeable film.

‡ Values are the mean of three replicate cells ± SE.

§ n = 1 cell.

was maintained in an atmosphere of constant RH for the duration of the test (i.e., days), which is not likely to occur under field conditions. Testing of films under conditions of very high RH may represent the worst-case scenario in terms of film permeability. Testing of films under conditions of high RH on one side and moderate humidity on the other may provide a reasonable representation of field behavior.

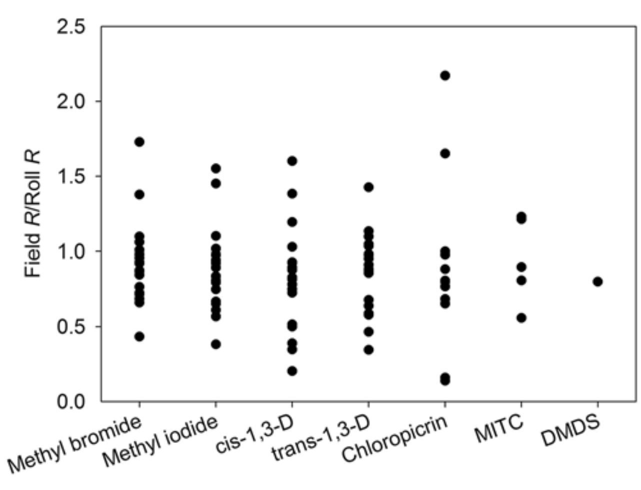

Fig. 5. Ratio of the response of the resistance (*R*) value determined for VIF <48 h after field installation to that determined with no field handling (sample taken directly from the roll of film). All values determined at 25°C. Chloropicrin results do not include films for which both *R* values were not quantifiable in these tests (Supplementary Table S4). DMDS, dimethyl disulfide; MITC, methyl isothiocyanate.

In a previous study, field deployment of a VIF decreased its permeability to CP to approximately the same as that for LDPE (Qin et al., 2008). This large change in permeability was implicated in the failure of the VIF to control emissions of drip-applied CP (Qin et al., 2008). In another field study, estimated emissions of MeBr were about the same in bedded systems using HDPE and Hytibar tarps (Wang and Yates, 1998). In our studies, changes in film permeability due to increases in temperature or field installation were generally less than a factor of five, which is unlikely to produce such a drastic increase in fumigant emissions. Other factors, such as fumigant emissions from bare furrows in fields in which only the bed is tarped (Papiernik et al., 2004; Qin et al., 2008) and emissions from glued VIF seams (Gao et al., this issue), are also unlikely to reduce the effectiveness of VIF to that of a polyethylene film. Of the factors that have been investigated, the strong dependence of VIF R values on relative humidity seems to be a probable mechanism whereby fumigant flux through an intact tarp of expected low permeability is much higher than anticipated.

Multilayer films that sandwich a high-barrier film between two polyethylene layers might show variable resistance to the effects of water sorption in the interlayer, depending on the kinetics of water transport through the polyethylene film. Water sorption depresses the glass transition temperature of polymers, which affects their permeability to gases (Eichler and Miltz, 1993). For ethylene vinyl alcohol, the glass transition temperature is 20 to 40°C at intermediate relative humidity (Zhang et al., 1999), suggesting that the

Table 2. Resistance to diffusion (R) of a virtually impermeable film (FM4) at different relative humidity.

Relative humidity†	R value				
	Methyl bromide	Methyl iodide	cis-1,3-D	trans-1,3-D	Chloropicrin
	h cm^{-1}				
100% source, 100% receiving	13.8 ± 0.6‡	11.7 ± 0.6	3.5 ± 0.2	1.9 ± 0.1	16 ± 1
100% source, 36% receiving	25 ± 3	23 ± 3	9 ± 2	5.9 ± 0.9	34 ± 7
2% source, 100% receiving	25 ± 3	23 ± 3	10 ± 2	5.8 ± 0.9	45 ± 6
2% source, 2% receiving	3000 ± 3000	14,000 ± 5000	50,000 ± 1000	14,000 ± 2000	33,000 ± 2000

† Initial distribution of water vapor in source cell and receiving cell.

‡ Values are the mean of triplicate cells ± SE.

permeability of films composed of ethylene vinyl alcohol may be especially susceptible to changes in humidity at environmentally relevant temperatures. Additional research is needed to more fully characterize the effects of water vapor on the permeability of VIF to fumigant vapors and to develop advanced films that reliably reduce emissions under a variety of field conditions.

Estimating Test Duration

The length of a permeability test depends on how quickly the source and receiving cells reach equilibrium. Because true equilibrium is approached asymptotically, requiring nearly infinite time, a test is considered operationally complete when the ratio of the concentration in the receiving chamber is some fraction of the source chamber (e.g., 95% of equilibrium). For impermeable films, especially those tested under low RH conditions, the time to equilibrium may be so large that the test duration becomes impractical and the test is ended without reaching near-equilibrium. Therefore, the time needed to conduct a test depends on the R value of the film–chemical combination and an arbitrary target point for the percent of equilibrium. If the R value is known or can be estimated, the time needed to reach a specified fraction of equilibrium can be obtained using

$$t_0 = \frac{LR_o}{2}\ln\left[\frac{1+f}{1-f}\right] \quad [2]$$

where R_o is the estimated film resistance coefficient (R = $1/h$), L is the half-thickness of the permeability cell (L = thickness of source side = thickness of receiving side), and f is the equilibrium fraction, defined as

$$f = \frac{C_r(t_0)}{C_s(t_0)}; \qquad 0 \le f \le 1 \quad \text{(1 at equilibrium)} \quad [3]$$

where C_s and C_r are the fumigant concentrations in the source and receiving cells, respectively. At early times, $f \approx 0$, and as equilibrium is approached, $f \approx 1$. Equation [2] assumes there is no sorption of the fumigant to the film (i.e., $k_p = 0$), that the system parameter α is zero, and that the $L = L_s = L_r$ (see Papiernik et al., 2001). Equation [2] can be used to estimate the duration required for a specific permeability test. For our systems, which use an L of 4 cm, the time required to achieve 95% equilibrium is 7 h for a film with an R = 1 (similar to the polyethylene films tested), 3 d for films with R = 10, and 30 d for a film with R = 100 (some of the VIF tested). For a VIF with an R value of 1000, the C_r at the end of a 30 d test will be 18% of the C_s, assuming that k_p and α are zero. For the films reported here, α and k_p values ranged from 0 to >100, but setting these terms to zero in the model regression produced a <10% change in R values, as has been previously reported (Papiernik et al., 2001). For the film–fumigant combinations tested, determinations of R values were relatively insensitive to fumigant sorption to the film, indicating that estimates of the duration required for a test should not be strongly affected by assuming no sorption.

Equation [2] was also used to estimate a lower limit for R values for a small number of tests of low-permeability films that did not produce a reliable quantification of R (Tables S2–S4). These estimates used the maximum C_r/C_s observed in any cell as f and the duration of the experiment as t_0. Using Eq. [2] with the results of a long-term incubation allows for an estimate of the lower limit of R values in tests in which concentrations remain very low in the receiving chamber throughout the experiment.

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